

Collinear scattering of photoexcited carriers in graphene

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We propose an explicitly solvable model for collinear scattering of photoexcited carriers in intrinsic graphene irradiated by monochromatic light. We find that the collinear scattering rate is directly proportional to the photocarrier energy and derive an analytic expression for the corresponding relaxation time. The result agrees with the recent numerical prediction [Mihnev *et al.* Nat. Commun. **7**, 11617 (2016)] and is able to describe the photocarrier evolution at low energies, where scattering on optical phonons is strongly suppressed.

I. INTRODUCTION

Graphene represents a single layer of carbon atoms exfoliated from bulk graphite¹ or grown by the chemical vapor deposition (CVD) technique.² This material offers many extraordinary properties to exploit in optoelectronics such as universal (frequency-independent) absorption of light and overall low opacity,³ excellent electrical⁴ and thermal⁵ conductivity. Possible applications include transparent electrodes in displays and photovoltaic modules,⁶ high-speed electronic⁷ and optical⁸ devices, energy storage⁹, and many more.¹⁰ The unconventional optoelectronic properties of graphene are related to its extremely peculiar electronic spectrum: The charge carriers demonstrate linear energy dispersion and there is no band gap between conduction and valence bands.¹¹ The combination of both is an exception among conducting materials¹² and may offer innovative applications not possible within conventional approaches. In particular, zero band gap means that the photocarriers can easily be excited even by using THz radiation,^{13–15} when optical phonon emission is strongly suppressed and noncollinear carrier-carrier scattering turns out to be remarkably slow.¹⁵ Our hypothesis is that the photocarrier evolution is governed by collinear electron-electron (e-e) scattering, when all photocarrier momenta involved are *parallel*.^{16–18} This is not possible in conventional semiconductors with the parabolic dispersion for carriers because momentum- and energy-balance equations cannot be satisfied in such processes simultaneously. In contrast with previous approaches devoted to this problem,^{16–24} the present work aims for an explicitly solvable model.

The reason why a collinear e-e scattering channel may dominate in photocarrier relaxation is threefold. First, pseudospin conservation results in partial suppression of e-e scattering with a non-zero scattering angle and even leads to complete suppression in the case of backscattering.¹⁸ This has been confirmed theoretically²⁵ and proven experimentally.^{15,26,27} Second, collinear electrons remain collinear even though they may exchange momenta. Hence, they maintain a stable collinear scattering channel until a noncollinear electron comes into play. Third, thanks to the constant velocity, the distance between collinear electrons does not change while they interact with each other. As a consequence, collinear carriers “spend a lot of time together”¹⁸ and, therefore,

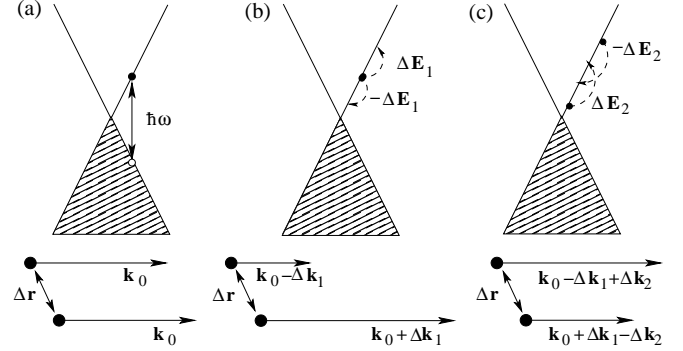


FIG. 1. Collinear scattering in momentum and real space. (a) Collinear photocarriers excited by monochromatic light with frequency ω have the same momentum k_0 . (b,c) Collinear photoelectrons remain collinear while interacting with each other. Most important, the distance between these electrons does not change, because they travel with the same speed due to the linear dispersion. Hence, the two-particle interaction potential $V(\mathbf{r})$ contributes at $\mathbf{r} = \Delta\mathbf{r}$ only and can be taken equal to zero otherwise.

e-e interactions along graphene’s conical bands are much more efficient than across. Last but not least, there is a recent experimental evidence¹⁵ of remarkably slow non-collinear e-e scattering obtained by means of pump-probe spectroscopy performed at the excitation energies below the optical phonon energy. These observations all together suggest that the full two-dimensional (2D) collision integral can be reduced to its one-dimensional (1D) analog for the sake of simplicity. In what follows, we derive an explicit formula for collinear relaxation time τ_{coll} describing thermalization of photoelectrons excited by monochromatic light of frequency ω , as shown in Fig. 1. The photocarrier relaxation rate reads

$$\frac{1}{\tau_{\text{coll}}} = \frac{\tilde{\alpha}^2 E}{4\pi^3 \hbar} \ln \left(\frac{1}{\tilde{\alpha}} \right), \quad (1)$$

where E is the photocarrier energy counted from the neutrality point, $\tilde{\alpha} = e^2/(\epsilon\hbar v)$ is the effective fine-structure constant for carriers in graphene determined by the electron charge e , Plank constant \hbar , effective dielectric constant ϵ , and carrier velocity v . To derive Eq. (1) we employed the renormalization procedure²⁸ based on the perturbation theory valid for $\tilde{\alpha} < 1$. For graphene

on the most conventional substrates, $\tilde{\alpha}$ is typically between 0.3 and 0.8; see Fig. 3. Hence, the photocarrier relaxation time scales with the photocarrier energy as $\tau_{\text{coll}} \sim 1 \text{ ps} \cdot \text{eV}/E$, which is in perfect agreement with the recent numerical result; see Fig. 6 in Ref. 24. In Section II we derive Eq. (1) and wrap up in Section III by discussing its physical consequences.

II. MODEL

A. Preliminaries

The carriers in graphene near the K-point of the first Brillouin zone are described by the massless Dirac Hamiltonian $H_0 = \hbar v \hat{\sigma} \cdot \mathbf{k}$, where $\hbar \mathbf{k}$ is the two-component momentum operator, $\hat{\sigma}$ is the pseudospin operator constructed out of the Pauli matrices, and v is the carrier velocity determined by the tight-binding parameters for electrons on the honeycomb lattice. The eigenstates of H_0 are given by $\varphi_{\mathbf{k}s}(\mathbf{r}) = \frac{1}{L\sqrt{2}} e^{i\mathbf{k}\mathbf{r}} (1, s e^{i\theta})^T$, where $s = \pm 1$ is the band (or pseudospin) index, $\tan \theta = k_y/k_x$ is the direction of motion, \mathbf{r} is the two-component particle position, and L is the sample size. The eigenvalues of H_0 are $E_s = s\hbar v k$. The two-particle wave function can be constructed out of $\varphi_{\mathbf{k}s}(\mathbf{r})$ as

$$\psi_{\mathbf{k}_i s_i \mathbf{k}_j s_j} = \frac{1}{\sqrt{2}} [\varphi_{\mathbf{k}_i s_i}(\mathbf{r}_i) \varphi_{\mathbf{k}_j s_j}(\mathbf{r}_j) - \varphi_{\mathbf{k}_i s_i}(\mathbf{r}_j) \varphi_{\mathbf{k}_j s_j}(\mathbf{r}_i)]. \quad (2)$$

The probability for a given particle to occupy a given one-particle state with (\mathbf{k}, s) is described by the distribution function $f_{\mathbf{k}s}$ which satisfies the following differential equation¹⁸

$$\begin{aligned} \frac{df_{\mathbf{k}_1 s_1}}{dt} = & \frac{2\pi}{\hbar} \sum_{\mathbf{k}_2, \mathbf{k}_3, \mathbf{k}_4} \sum_{s_2, s_3, s_4} w(\mathbf{k}_1 s_1, \mathbf{k}_2 s_2; \mathbf{k}_3 s_3, \mathbf{k}_4 s_4) \\ & \times \delta(E_{s_1} + E_{s_2} - E_{s_3} - E_{s_4}) \\ & \times [(1 - f_{\mathbf{k}_1 s_1})(1 - f_{\mathbf{k}_2 s_2})f_{\mathbf{k}_3 s_3}f_{\mathbf{k}_4 s_4} \\ & - f_{\mathbf{k}_1 s_1}f_{\mathbf{k}_2 s_2}(1 - f_{\mathbf{k}_3 s_3})(1 - f_{\mathbf{k}_4 s_4})], \end{aligned} \quad (3)$$

where $w(\mathbf{k}_1 s_1, \mathbf{k}_2 s_2; \mathbf{k}_3 s_3, \mathbf{k}_4 s_4)$ describes interaction of two particles and includes a direct (Hartree) and an exchange (Fock) term in the form¹⁸

$$w(\mathbf{k}_1 s_1, \mathbf{k}_2 s_2; \mathbf{k}_3 s_3, \mathbf{k}_4 s_4) = \frac{1}{2} |V_{1234} - V_{1243}|^2 + |V_{1234}|^2. \quad (4)$$

Here,

$$\begin{aligned} V_{ijmn} = & \frac{1}{4} \left(1 + s_i s_m e^{i(\theta_m - \theta_i)} \right) \left(1 + s_j s_n e^{i(\theta_n - \theta_j)} \right) \\ & \times \int \frac{d^2 \mathbf{r}_1}{L^2} \int \frac{d^2 \mathbf{r}_2}{L^2} V(\mathbf{r}_2 - \mathbf{r}_1) e^{i(\mathbf{k}_m - \mathbf{k}_i)\mathbf{r}_1 + i(\mathbf{k}_n - \mathbf{k}_j)\mathbf{r}_2} \end{aligned} \quad (5)$$

with $V(\mathbf{r})$ being the interaction potential. The laws of pseudospin and momentum conservation are encoded in the first and second lines of Eq. (5) respectively. Eq. (3)

is valid for an arbitrary $V(\mathbf{r})$ and contains information about collinear as well as noncollinear scattering. It does not allow for an explicit solution in this general form, but provides the starting point for our model.

B. Initial photocarrier distribution

To solve Eq. (3) we need an initial condition for $f_{\mathbf{k}s}$. We suppose that $f_{\mathbf{k}s}$ at $t = 0$ is created by linearly polarized light and therefore anisotropic in momentum space. The anisotropy has been predicted theoretically^{25,29-31} and demonstrated experimentally.^{26,27,32} The light-carrier interaction is described by the Hamiltonian $H_{\text{int}} = \frac{e v}{c} \hat{\sigma} \cdot \mathbf{A}$, where $\mathbf{A} = \mathbf{A}_0 \cos(\omega t - qz)$ is the vector potential created by the linearly polarized electromagnetic wave $\mathbf{E} = \mathbf{E}_0 \sin(\omega t - qz)$ with ω being the radiation frequency, and $\mathbf{E}_0 = \frac{\omega \mathbf{A}_0}{c}$. We assume normal incidence $\mathbf{q} \perp \mathbf{k}$ so that there is no momentum transfer from photons to electrons. Due to the pseudospin selection rules²⁷ the photocarrier momenta are aligned perpendicular to the polarization plane of light. The e-e scattering also obeys pseudospin conservation and hence maintains anisotropy.²⁵

It has been shown in Ref. 27 that the initial photoelectron distribution $f_{\mathbf{k}s}(t = 0)$ created by a monochromatic pump pulse in intrinsic graphene is given by $f_{\mathbf{k}s}(0) = f_{\mathbf{k}s}^{(0)}(0) + f_{\mathbf{k}s}^{(1)}(0)$, where

$$f_{\mathbf{k}s}^{(0)}(0) = \frac{1}{1 + \exp(s\hbar v k/T_0)} \quad (6)$$

is the Fermi-Dirac function at the initial temperature T_0 and zero chemical potential, and

$$\begin{aligned} f_{\mathbf{k}s}^{(1)}(0) = & \frac{4\pi^2 \alpha v^2 \Phi}{\hbar \omega^2} \sin^2(\theta - \theta_{E_0}) \delta(\omega - \Omega) \\ & \times \left(f_{\mathbf{k}(-s)}^{(0)} - f_{\mathbf{k}(+s)}^{(0)} \right) \end{aligned} \quad (7)$$

is the nonequilibrium addition. Here, $\Phi = (cE_0^2 \delta t)/(8\pi)$ is the pump fluence with δt being the pulse duration, $\alpha = e^2/(\hbar c)$ is the fine-structure constant, $\hbar \Omega = 2\hbar v k$ is the interband transition energy, and $\tan \theta_{E_0} = E_{0y}/E_{0x}$. Since the initial temperature is low as compared with $\hbar \omega$ we can set $(f_{\mathbf{k}(-s)}^{(0)} - f_{\mathbf{k}(+s)}^{(0)}) = s$. To take into account the finite spectral width of the pump pulse, the delta function can be substituted by a Gaussian distribution of the width $\Delta\omega$, i.e., $\delta(\omega - \Omega) \rightarrow \delta_{\Delta\omega}(\omega - \Omega)$, where

$$\delta_{\Delta\omega}(\omega - \Omega) = \frac{1}{\sqrt{2\pi}\Delta\omega} e^{-\frac{(\omega - \Omega)^2}{2(\Delta\omega)^2}}. \quad (8)$$

C. Collinear limit

In this subsection we simplify our model in order to investigate possible manifestations of collinear scattering. We set a certain direction of motion in Eq. (3) and employ

dimensionless 1D momenta $\xi = k/k_0$, where $k_0 = \omega/2v$ is the central wave vector of photoexcited electrons and holes. Note, that $-\infty < \xi < \infty$, and the energy dispersion is then given by $E_\xi = \hbar\omega\xi/2$. There is no band index anymore because the conduction- and valence-band states are distinguished by the sign of ξ . The initial distribution given by the sum of Eqs. (6) and (7) in the dimensionless units is written as $f_\xi(0) = f_\xi^{(0)}(0) + f_\xi^{(1)}(0)$, where

$$f_\xi^{(0)}(0) = \frac{1}{1 + \exp(\beta_0\xi)}, \quad \beta_0 = \frac{\hbar v k_0}{T_0}, \quad (9)$$

$$f_\xi^{(1)}(0) = \eta [\delta(1 - \xi) - \delta(1 + \xi)], \quad \eta = \frac{n_{\text{ph}}}{n_0} \sin^2(\theta - \theta_{E_0}). \quad (10)$$

Here, $n_0 = k_0^2/\pi$, and $n_{\text{ph}} = \pi\alpha\Phi/(\hbar\omega)$ is the 2D photocarrier concentration with $\pi\alpha$ being the linear optical absorption of graphene with the valley and spin degeneracy taken into account. The first term in Eq. (10) corresponds to population of the conduction-band states, whereas the second one describes depopulation of the valence-band states. We can take into account the spectral width $\Delta\omega$ in a way similar to Eq. (8), i.e., the delta-functions in Eq. (10) can be substituted by

$$\delta_\sigma(1 \pm \xi) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{(1 \pm \xi)^2}{2\sigma^2}}, \quad (11)$$

where $\sigma = \Delta\omega/\omega$.

Since the distance between interacting collinear electrons does not change we approximate the collinear interaction potential by a point-like one $V(\mathbf{r}) = u_0\delta(\mathbf{r} - \Delta\mathbf{r})$, where u_0 is a constant independent of spatial coordinates, and $\Delta\mathbf{r}$ is the e-e mean distance that cancels out at the end of the day. The scattering probability then reads

$$w(\mathbf{k}_1 s_1, \mathbf{k}_2 s_2; \mathbf{k}_3 s_3, \mathbf{k}_4 s_4) = \delta(\mathbf{k}_3 + \mathbf{k}_4 - \mathbf{k}_1 - \mathbf{k}_2) \quad (12)$$

$$\times \frac{\pi^2 u_0^2}{L^6} [1 + s_1 s_3 \cos(\theta_3 - \theta_1)] [1 + s_2 s_4 \cos(\theta_4 - \theta_2)],$$

where the delta function represents momentum conservation. Transforming the collision integral (3) into a 1D form is not a trivial task because the laws of energy and momentum conservation result in the delta-function squared, which is not a well-defined function. To overcome the difficulties associated with this divergence we employ the renormalization procedure²⁸ outlined in Appendix A. Finally, we transform the sums over k_i in Eq. (3) to the integrals over ξ_i and obtain the following equation describing collinear scattering:

$$\frac{df_{\xi_1}}{d\tau} = \int_{-\infty}^{\infty} d\xi_3 \int_{-\infty}^{\infty} d\xi_4 \sqrt{\frac{\xi_4 \xi_3 (\xi_3 + \xi_4 - \xi_1)}{\xi_1}} \quad (13)$$

$$\times [(1 - f_{\xi_1})(1 - f_{\xi_3 + \xi_4 - \xi_1}) f_{\xi_3} f_{\xi_4} - f_{\xi_1} f_{\xi_3 + \xi_4 - \xi_1} (1 - f_{\xi_3})(1 - f_{\xi_4})],$$

where $\tau = t/t_0$ is the dimensionless time with t_0^{-1} given by

$$t_0^{-1} = \frac{u_0^2 k_0^3}{2\pi^3 \hbar^2 v} \ln\left(\frac{1}{\alpha}\right). \quad (14)$$

D. Evolution of the photocarrier occupation

Eq. (13) is still too complicated for an analytic solution. Since monochromatic radiation determines a characteristic photoelectron wave vector k_0 we assume that all momenta involved in collinear scattering are of the order of k_0 , i.e., $\xi_i \sim 1$. If we just set $\xi_i = 1$ everywhere in the right-hand side of Eq. (13), then the solution is trivially zero ($f_\xi = 0$). Therefore, we assume $\xi_i = 1$ in the renormalization multiplier so that the ξ_i -dependence is retained in the carrier occupation alone. Hence, Eq. (13) can be written as

$$\frac{df_{\xi_1}}{d\tau} = \int_{-\infty}^{\infty} d\xi_3 \int_{-\infty}^{\infty} d\xi_4 [(1 - f_{\xi_1})(1 - f_{\xi_3 + \xi_4 - \xi_1}) f_{\xi_3} f_{\xi_4} - f_{\xi_1} f_{\xi_3 + \xi_4 - \xi_1} (1 - f_{\xi_3})(1 - f_{\xi_4})]. \quad (15)$$

This equation can be solved in the weak-excitation limit $\eta \ll 1$. The *Ansatz* can be written as $f_\xi(\tau) = f_\xi^{(0)}(\tau) + f_\xi^{(1)}(\tau)$, where

$$f_\xi^{(0)}(\tau) = \frac{1}{1 + \exp[\beta(\tau)\xi]}, \quad (16)$$

$$f_\xi^{(1)}(\tau) = \eta [\delta(1 - \xi) - \delta(1 + \xi)] e^{-c(\xi)\tau}. \quad (17)$$

Here, $\beta(\tau)$ and $c(\xi)$ are unknown functions to be determined. Obviously $\beta(\tau)$ must satisfy the initial condition $\beta(0) = \beta_0$, whereas $c(\xi)$ must be even $c(\xi) = c(-\xi)$. Since the excitation is weak we neglect the terms of the order of η^2 and η^3 , see Appendix B. Assuming the low-temperature limit $\beta \gg 1$ we take the integrals over $\xi_{3,4}$ and write Eq. (15) as

$$-\frac{\xi_1(d\beta/d\tau)}{4 \cosh^2(\beta\xi_1/2)} - \eta c(\xi_1) [\delta(1 - \xi_1) - \delta(1 + \xi_1)] e^{-c(\xi_1)\tau} \quad (18)$$

$$= 3\eta \left[\frac{-2}{1 + e^{\beta\xi_1}} + \frac{\xi_1 - 1}{e^{\beta(\xi_1 - 1)} - 1} + \frac{\xi_1 + 1}{1 - e^{\beta(\xi_1 + 1)}} \right] e^{-c(1)\tau}$$

$$- \eta \frac{\xi_1^2}{2} [\delta(1 - \xi_1) - \delta(1 + \xi_1)] e^{-c(\xi_1)\tau},$$

Comparing the left- and right-hand sides in Eq. (18) we find that $c(\xi) = \xi^2/2$. In order figure out $\beta(\tau)$ we employ the energy-balance equation for electrons which in our dimensionless units reads

$$\int_0^\infty d\xi \xi f_\xi(0) = \int_0^\infty d\xi \xi f_\xi(\tau). \quad (19)$$

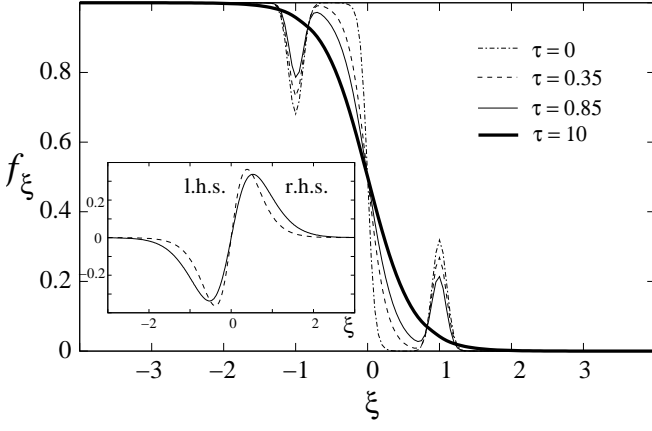


FIG. 2. Evolution of the nonequilibrium distribution function $f_\xi(\tau)$ given by Eq. (22) with $\eta = 0.08$ corresponding to $\Phi = 10 \mu\text{J}/\text{cm}^2$ at $\hbar\omega = 1 \text{ eV}$ or $\Phi = 0.01 \mu\text{J}/\text{cm}^2$ at $\hbar\omega = 100 \text{ meV}$. The delta-function is approximated by the Gaussian distribution (11) with $\sigma = 0.1$, and the normal polarization configuration is assumed, i.e., $\theta - \theta_{E_0} = \pi/2$. The carrier temperature rapidly increases with τ starting from $\beta_0 = 20$ (corresponds to the room temperature at $\hbar\omega = 1 \text{ eV}$) to $\beta \sim 4$ ($T \sim 1450 \text{ K}$). The inset shows that the right- and left-hand sides of Eq. (21) are approximately equal at $\beta = 4$.

The solution of Eq. (19) is given by

$$\beta(\tau) = \frac{\beta_0}{\sqrt{1 + \frac{12\beta_0^2\eta}{\pi^2}(1 - e^{-\tau/2})}}. \quad (20)$$

The temperature for holes is the same as for electrons in intrinsic graphene. Substituting Eq. (20) and $c(\xi) = \xi^2/2$ into Eq. (18) the latter reduces to the following relation

$$\frac{\xi_1\beta^3}{4\pi^2 \cosh^2(\beta\xi_1/2)} = \frac{-2}{1 + e^{\beta\xi_1}} + \frac{\xi_1 - 1}{e^{\beta(\xi_1-1)} - 1} + \frac{\xi_1 + 1}{1 - e^{\beta(\xi_1+1)}}, \quad (21)$$

which approximately holds at reasonable $\beta > 1$; see inset in Fig. 2. Indeed, both sides of Eq. (21) decay exponentially at $\beta \rightarrow \infty$ for $|\xi_1| > 1$ and vanish completely at $\xi_1 \rightarrow \pm\infty$ or $\xi_1 = 0$ for any finite β . Hence, the approximate solution of Eq. (15) at $\eta \ll 1$ and $\beta \gg 1$ reads

$$f_\xi(\tau) = \frac{1}{1 + \exp[\beta(\tau)\xi]} + \eta[\delta(1 - \xi) - \delta(1 + \xi)]e^{-\xi^2\frac{\tau}{2}}, \quad (22)$$

with $\beta(\tau)$ given by Eq. (20). From Eq. (22) one can deduce the dimensionless relaxation rate $\xi^2/2$ that approximately equals $1/2$ at $\xi \sim 1$. The distribution function $f_\xi(\tau)$ is depicted in Fig. 2 for different τ .

III. DISCUSSION AND CONCLUSION

The explicit solution (22) has been derived by assuming that $\xi \sim 1$, i.e., $k \sim k_0$. Hence, all the quantities involved should also be evaluated having in mind this approximation. In particular, u_0 should mimic the Fourier

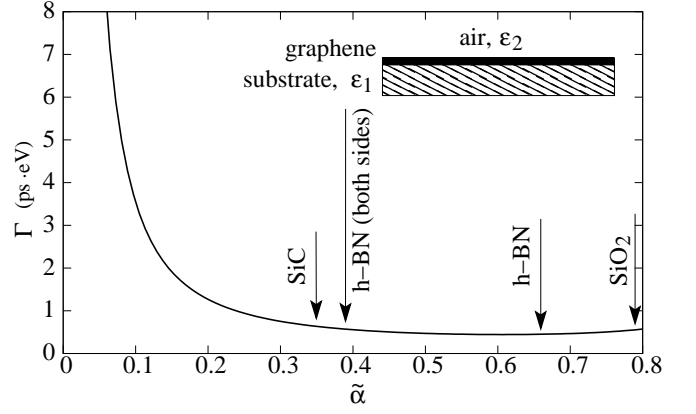


FIG. 3. The photocarrier relaxation parameter (24) as a function of the effective fine-structure constant $\tilde{\alpha} = e^2/(\epsilon\hbar v)$, where $\epsilon = (\epsilon_1 + \epsilon_2)/2$ is tunable by changing the substrate. Arrows indicate positions for different substrates routinely used in graphene optoelectronic devices.

transform of the Coulomb potential taken at $k \sim k_0$, i.e., $u_0 = e^2/\epsilon k_0$. As consequence, t_0 takes the form

$$t_0 = \frac{4\pi^3}{\tilde{\alpha}^2\omega \ln(1/\tilde{\alpha})}. \quad (23)$$

In this approximation, the photocarrier energy is $E = \hbar v k_0 \equiv \hbar\omega/2$, and the relaxation time deduced from Eq. (22) reads $\tau_{\text{coll}} = 2t_0$. The result can be represented either by Eq. (1) or in the form $\tau_{\text{coll}} = \Gamma/E$, where Γ is given by

$$\Gamma = \frac{4\pi^3\hbar}{\tilde{\alpha}^2 \ln(1/\tilde{\alpha})}, \quad (24)$$

and shown in Fig. 3 for different substrates. The effective dielectric constant ϵ for graphene on a substrate is given by $\epsilon = (\epsilon_1 + \epsilon_2)/2$, where ϵ_1 and ϵ_2 are the relative permittivity of the material below and above graphene layer, respectively.³³ For air, SiO₂, BN, and SiC the static relative permittivity is given by 1, 3.9, 5.06, and 10.03 respectively.^{33–35} The carrier velocity is assumed to be $v = 1.1 \times 10^8 \text{ cm/s}$.³³

The photocarrier relaxation time $\tau_{\text{coll}} = \Gamma/E$ with Γ shown in Fig. 3 is the main result of this work. Our outcomes are in perfect agreement with the recent numerical result,²⁴ where calculations have been performed in full 2D momentum space with all collinear and non-collinear e-e scattering processes included. The numerical solution²⁴ suggests $\Gamma \approx 0.9 \text{ eV} \cdot \text{ps}$, cf. Fig. 3 above. Our model provides an *explicit* expression for this parameter. Most important, the agreement between the full 2D model and our approximate 1D approach suggests that collinear e-e collisions *indeed* dominate photocarrier thermalization as long as the optical phonon emission is suppressed. The most likely reason is the stability of collinear scattering channel explained in Introduction.

Our model can also qualitatively predict the evolution of a Gaussian photocarrier distribution created by an im-

pulsive optical excitation. Since Eq. (1) suggests that the photocarriers with higher energies thermalize faster, any initially symmetric Gaussian distribution becomes asymmetric with the maximum shifted towards the neutrality point. This is what one can see in Refs. 18 and 25: The electron distribution loses its Gaussian form and drifts towards the neutrality point while evolving in momentum space. The particular reshaping of the photocarrier distribution depends on the model for e-e screening.

The model proposed above can be assessed by measuring photocarrier evolution using optical pump-probe spectroscopy well-established for graphene.^{15,21,26,27,36–42} The most relevant experimental setup has been realized very recently by König-Otto *et al.* in Ref. 15, where measurements have been performed at the excitation energy below the optical phonon emission threshold. Besides thermalization time, the hot carrier temperature can also be measured. The temperature can be deduced from Eq. (20) and in energy units reads

$$T_{1D} = \sqrt{T_0^2 + \frac{12\alpha\hbar^2 v^2 \Phi}{\hbar\omega} \sin^2(\theta - \theta_{E_0}) \left(1 - e^{-\frac{t}{\tau_0}}\right)}. \quad (25)$$

In the case of unpolarized light, $\sin^2(\theta - \theta_{E_0})$ should be substituted by $1/2$. Eq. (25) in the limit $t \rightarrow \infty$ differs from the conventional estimation⁴³ based on the energy-balance equation in intrinsic graphene neglecting phonon emission. In our notations, the conventional estimation can be written as

$$T_{2D} = \left(T_0^3 + \frac{\pi^2 \alpha \hbar^2 v^2 \Phi}{6\zeta(3)}\right)^{\frac{1}{3}}, \quad (26)$$

where ζ is the Riemann zeta function. The most striking difference between Eqs. (25) and (26) appears in the ω -dependence: Eq. (25) diverges at $\omega \rightarrow 0$, whereas Eq. (26) does not. The difference arises because, in our case, the photocarriers are not yet thermalized over the whole two-dimensional momentum space. For a more precise evaluation of the photocarrier temperature, noncollinear e-e scattering and phonon emission should be taken into account.²⁷

To conclude, we have developed an explicitly solvable model for photocarrier thermalization due to collinear e-e scattering in graphene. The model predicts $1/E$ scaling of collinear e-e relaxation time that suggests its importance for thermalization in the high-energy tail of a photoelectron distribution. Note that this high-energy tail plays a leading role in thermionic emission across silicon-graphene Schottky barriers⁴⁴ or graphene-isolator-graphene heterostructures.^{45,46} This paves the way towards correct assessment of the photocarrier thermalization dynamics in graphene-based optoelectronic devices.^{47,48}

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Appendix A: Collision integral in collinear limit

Here, we follow Ref.²⁸ to write our collision integral in the collinear limit. We start from Eqs. (3) and (12), change the sums to integrals as $\sum_{k_i} \rightarrow \int d^2 k_i L^2 / (2\pi)^2$, and make use of the delta-function in Eq. (12) to integrate over \mathbf{k}_2 . The result reads

$$\begin{aligned} \frac{df_{k_1}}{dt} = & \frac{u_0^2}{(2\pi)^3 \hbar^2 v} \int dk_3 \int dk_3^\perp \int dk_4 \int dk_4^\perp \\ & \times \delta(|\mathbf{k}_1| + |\mathbf{k}_3 + \mathbf{k}_4 - \mathbf{k}_1| - |\mathbf{k}_3| - |\mathbf{k}_4|) \\ & \times [(1 - f_{k_1})(1 - f_{k_3+k_4-k_1})f_{k_3}f_{k_4} \\ & - f_{k_1}f_{k_3+k_4-k_1}(1 - f_{k_3})(1 - f_{k_4})], \end{aligned} \quad (A1)$$

where $k_{3,4}^\perp$ are the components of $\mathbf{k}_{3,4}$ perpendicular to the collinear channel. They are set to zero in the distribution functions as well as in the pseudospin form-factor. It is convenient to introduce the variable $\mathbf{q} = \mathbf{k}_3 - \mathbf{k}_1$ and assume that $\mathbf{k}_1 = (k_1, 0)$, $\mathbf{k}_4 = (k_4, k_\perp)$, $\mathbf{q} = (q, q_\perp)$. Since the perpendicular components are small we can utilize the following approximate expressions:

$$|\mathbf{k}_1 + \mathbf{q}| \approx k_1 + q + \frac{1}{2} \frac{q_\perp^2}{k_1 + q}, \quad (A2)$$

$$|\mathbf{k}_4 + \mathbf{q}| \approx k_4 + q + \frac{1}{2} \frac{(k_\perp + q_\perp)^2}{k_4 + q}, \quad (A3)$$

$$|\mathbf{k}_4| \approx k_4 + \frac{1}{2} \frac{k_\perp^2}{k_4}. \quad (A4)$$

The delta-function can then be written as

$$\begin{aligned} \delta(|\mathbf{k}_1| + |\mathbf{q} + \mathbf{k}_4| - |\mathbf{k}_1 + \mathbf{q}| - |\mathbf{k}_4|) = & \quad (A5) \\ 2\delta\left(q_\perp^2 \frac{k_1 - k_4}{(k_1 + q)(k_4 + q)} + q_\perp \frac{2k_\perp}{k_4 + q} - \frac{k_\perp^2 q}{k_4(k_4 + q)}\right) \\ = & \left| \frac{2(k_4 + q)(k_1 + q)}{(k_1 - k_4)(q_\perp^{(2)} - q_\perp^{(1)})} \right| \left[\delta(q_\perp - q_\perp^{(1)}) + \delta(q_\perp - q_\perp^{(2)}) \right], \end{aligned}$$

where $q_\perp^{(1)}$ and $q_\perp^{(2)}$ are the roots of the argument of the delta-function. The integral over q_\perp becomes trivial, and Eq. (A1) can be written as

$$\begin{aligned} \frac{df_{k_1}}{dt} = & \frac{2u_0^2}{(2\pi)^3 \hbar^2 v} \int \frac{dk_\perp}{|k_\perp|} \\ & \times \int dk_3 \int dk_4 \sqrt{\frac{k_4 k_3 (k_4 + k_3 - k_1)}{k_1}} \\ & \times [(1 - f_{k_1})(1 - f_{k_3+k_4-k_1})f_{k_3}f_{k_4} \\ & - f_{k_1}f_{k_3+k_4-k_1}(1 - f_{k_3})(1 - f_{k_4})]. \end{aligned} \quad (A6)$$

The integral over k_\perp diverges but this divergence is cut off by self-energy corrections. As discussed in Ref. 28, the

important range of the k_\perp integral is between $T/(\hbar v)$ and $\tilde{\alpha}T/(\hbar v)$, which results in $\int dk_\perp/k_\perp \approx 2 \ln(1/\tilde{\alpha})$. Finally,

we substitute k_i and t by corresponding dimensionless quantities ξ_i and τ and arrive at Eq. (13).

Appendix B: One-dimensional collision integral in detail

Assuming that $f_\xi^{(0)}(\tau)$ and $f_\xi^{(1)}(\tau)$ are given by Eqs. (16) and (17), respectively, the collision integral in Eq. (15) can be written as

$$\begin{aligned} & \int_{-\infty}^{\infty} d\xi_3 \int_{-\infty}^{\infty} d\xi_4 [(1 - f_{\xi_1})(1 - f_{\xi_3+\xi_4-\xi_1})f_{\xi_3}f_{\xi_4} - f_{\xi_1}f_{\xi_3+\xi_4-\xi_1}(1 - f_{\xi_3})(1 - f_{\xi_4})] = \\ & \int_{-\infty}^{\infty} d\xi_3 \int_{-\infty}^{\infty} d\xi_4 \left\{ f_{\xi_3}^{(1)} \left[\frac{1}{(1 + e^{-\beta\xi_1})(1 + e^{-\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{\beta\xi_4})} + \frac{1}{(1 + e^{\beta\xi_1})(1 + e^{\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{-\beta\xi_4})} \right] + \right. \\ & + f_{\xi_4}^{(1)} \left[\frac{1}{(1 + e^{-\beta\xi_1})(1 + e^{-\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{\beta\xi_3})} + \frac{1}{(1 + e^{\beta\xi_1})(1 + e^{\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{-\beta\xi_3})} \right] - \\ & - f_{\xi_1}^{(1)} \left[\frac{1}{(1 + e^{-\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{\beta\xi_3})(1 + e^{\beta\xi_4})} + \frac{1}{(1 + e^{\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{-\beta\xi_3})(1 + e^{-\beta\xi_4})} \right] - \\ & \left. - f_{\xi_3+\xi_4-\xi_1}^{(1)} \left[\frac{1}{(1 + e^{-\beta\xi_1})(1 + e^{\beta\xi_3})(1 + e^{\beta\xi_4})} + \frac{1}{(1 + e^{\beta\xi_1})(1 + e^{-\beta\xi_3})(1 + e^{-\beta\xi_4})} \right] + o^2(\eta) \right\}. \end{aligned} \quad (B1)$$

Some integrals in Eq. (B1) are calculated by utilizing the $\delta(1 \pm \xi_i)$ -functions in f_{ξ_i} , and Eq. (15) takes the form

$$\begin{aligned} \frac{df_{\xi_1}}{d\tau} &= 3\eta e^{-c(1)\tau} \int_{-\infty}^{\infty} \frac{d\xi_4 \sinh \beta}{\cosh [(\xi_4 - \xi_1)\beta] + \cosh \beta} \left[\frac{1}{(1 + e^{-\beta\xi_1})(1 + e^{\beta\xi_4})} - \frac{1}{(1 + e^{\beta\xi_1})(1 + e^{-\beta\xi_4})} \right] \\ &- f_{\xi_1}^{(1)} \int_{-\infty}^{\infty} d\xi_3 \int_{-\infty}^{\infty} d\xi_4 \left[\frac{1}{(1 + e^{-\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{\beta\xi_3})(1 + e^{\beta\xi_4})} + \frac{1}{(1 + e^{\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{-\beta\xi_3})(1 + e^{-\beta\xi_4})} \right]. \end{aligned} \quad (B2)$$

The first integral in Eq. (B2) can be calculated explicitly as

$$\int_{-\infty}^{\infty} \frac{d\xi_4 \sinh \beta}{\cosh [(\xi_4 - \xi_1)\beta] + \cosh \beta} \left[\frac{1}{(1 + e^{-\beta\xi_1})(1 + e^{\beta\xi_4})} - \frac{1}{(1 + e^{\beta\xi_1})(1 + e^{-\beta\xi_4})} \right] = \frac{-2}{1 + e^{\beta\xi_1}} + \frac{\xi_1 - 1}{e^{\beta(\xi_1-1)} - 1} + \frac{\xi_1 + 1}{1 - e^{\beta(\xi_1+1)}}.$$

The second (double) integral can also be calculated analytically for $\xi_1 > 0$ and $\xi_1 < 0$ and the outcome represents a combination of logarithmic and polylogarithmic functions with the arguments containing $1 - e^{\pm\beta\xi_1}$. If we assume that $\beta \gg 1$, then $1 - e^{\beta\xi_1} \approx -e^{\beta\xi_1}$ and $1 - e^{-\beta\xi_1} \approx 1$ for $\xi_1 > 0$ and vice versa for $\xi_1 < 0$. In this approximation the integral takes a simple form

$$\int_{-\infty}^{\infty} d\xi_3 \int_{-\infty}^{\infty} d\xi_4 \left[\frac{1}{(1 + e^{-\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{\beta\xi_3})(1 + e^{\beta\xi_4})} + \frac{1}{(1 + e^{\beta(\xi_3+\xi_4-\xi_1)})(1 + e^{-\beta\xi_3})(1 + e^{-\beta\xi_4})} \right] = \frac{\xi_1^2}{2}.$$

By using these expressions and calculating $\frac{df_{\xi_1}}{d\tau}$ we transform Eq. (B2) to Eq. (18) in the main text.

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¹ K. S. Novoselov, D. Jiang, F. Schedin, T. J. Booth, V. V. Khotkevich, S. V. Morozov, and A. K. Geim, Proceedings of the National Academy of Sciences of the United States

of America **102**, 10451 (2005).

² S. Bae, H. Kim, Y. Lee, X. Xu, J.-S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. Ri Kim, Y. I. Song, Y.-J. Kim, K. S. Kim, B. Ozyilmaz, J.-H. Ahn, B. H. Hong, and

- S. Iijima, *Nat Nano* **5**, 574 (2010).
- ³ R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, and A. K. Geim, *Science* **320**, 1308 (2008).
 - ⁴ K. Bolotin, K. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim, and H. Stormer, *Solid State Communications* **146**, 351 (2008).
 - ⁵ A. A. Balandin, S. Ghosh, W. Bao, I. Calizo, D. Teweldebrhan, F. Miao, and C. N. Lau, *Nano Letters* **8**, 902 (2008).
 - ⁶ L. G. D. Arco, Y. Zhang, C. W. Schlenker, K. Ryu, M. E. Thompson, and C. Zhou, *ACS Nano* **4**, 2865 (2010).
 - ⁷ Y.-M. Lin, C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, and P. Avouris, *Science* **327**, 662 (2010).
 - ⁸ M. Liu, X. Yin, E. Ulin-Avila, B. Geng, T. Zentgraf, L. Ju, F. Wang, and X. Zhang, *Nature* **474**, 64 (2011).
 - ⁹ Y. Zhu, S. Murali, M. D. Stoller, K. J. Ganesh, W. Cai, P. J. Ferreira, A. Pirkle, R. M. Wallace, K. A. Cychosz, M. Thommes, D. Su, E. A. Stach, and R. S. Ruoff, *Science* **332**, 1537 (2011).
 - ¹⁰ A. C. Ferrari, F. Bonaccorso, V. Fal'ko, K. S. Novoselov, S. Roche, P. Boggild, S. Borini, F. H. L. Koppens, V. Palermo, N. Pugno, J. A. Garrido, R. Sordan, A. Bianco, L. Ballerini, M. Prato, E. Lidorikis, J. Kivioja, C. Marinelli, T. Ryhanen, A. Morpurgo, J. N. Coleman, V. Nicolosi, L. Colombo, A. Fert, M. Garcia-Hernandez, A. Bachtold, G. F. Schneider, F. Guinea, C. Dekker, M. Barbone, Z. Sun, C. Galiotis, A. N. Grigorenko, G. Konstantatos, A. Kis, M. Katsnelson, L. Vandersypen, A. Loiseau, V. Morandi, D. Neumaier, E. Treossi, V. Pellegrini, M. Polini, A. Tredicucci, G. M. Williams, B. Hee Hong, J.-H. Ahn, J. Min Kim, H. Zirath, B. J. van Wees, H. van der Zant, L. Occhipinti, A. Di Matteo, I. A. Kinloch, T. Seyller, E. Quesnel, X. Feng, K. Teo, N. Rupasinghe, P. Hakonen, S. R. T. Neil, Q. Tannock, T. Lofwander, and J. Kinaret, *Nanoscale* **7**, 4598 (2015).
 - ¹¹ E. McCann, *Graphene Nanoelectronics: Metrology, Synthesis, Properties and Applications, chapter 8* (Springer-Verlag Berlin Heidelberg, 2012) pp. pages 237–275.
 - ¹² A. K. Geim and K. S. Novoselov, *Nat. Mat.* **6**, 183 (2007).
 - ¹³ S. A. Jensen, Z. Mics, I. Ivanov, H. S. Varol, D. Turchinovich, F. H. L. Koppens, M. Bonn, and K. J. Tielrooij, *Nano Letters* **14**, 5839 (2014).
 - ¹⁴ A. Bacsı and A. Virosztek, *Phys. Rev. B* **87**, 125425 (2013).
 - ¹⁵ J. C. König-Otto, M. Mittendorff, T. Winzer, F. Kadi, E. Malic, A. Knorr, C. Berger, W. A. de Heer, A. Pashkin, H. Schneider, M. Helm, and S. Winnerl, *Phys. Rev. Lett.* **117**, 087401 (2016).
 - ¹⁶ F. Rana, *Phys. Rev. B* **76**, 155431 (2007).
 - ¹⁷ T. Winzer and E. Malić, *Phys. Rev. B* **85**, 241404 (2012).
 - ¹⁸ A. Tomadin, D. Brida, G. Cerullo, A. C. Ferrari, and M. Polini, *Phys. Rev. B* **88**, 035430 (2013).
 - ¹⁹ R. Kim, V. Perebeinos, and P. Avouris, *Phys. Rev. B* **84**, 075449 (2011).
 - ²⁰ L. Pirro, A. Girdhar, Y. Leblebici, and J.-P. Leburton, *Journal of Applied Physics* **112**, 093707 (2012).
 - ²¹ D. Brida, A. Tomadin, C. Manzoni, Y. J. Kim, A. Lombardo, S. Milana, R. R. Nair, K. S. Novoselov, A. C. Ferrari, G. Cerullo, and M. Polini, *Nat. Commun.* **4**, 1987 (2013).
 - ²² J. C. W. Song, K. J. Tielrooij, F. H. L. Koppens, and L. S. Levitov, *Phys. Rev. B* **87**, 155429 (2013).
 - ²³ Z. Mics, K.-J. Tielrooij, K. Parvez, S. A. Jensen, I. Ivanov, X. Feng, K. Mullen, M. Bonn, and D. Turchinovich, *Nat Commun* **6**, 7655 (2015).
 - ²⁴ M. T. Mihnev, F. Kadi, C. J. Divin, T. Winzer, S. Lee, C.-H. Liu, Z. Zhong, C. Berger, W. A. de Heer, E. Malic, A. Knorr, and T. B. Norris, *Nature Communications* **7**, 11617 (2016).
 - ²⁵ E. Malic, T. Winzer, and A. Knorr, *Applied Physics Letters* **101**, 213110 (2012).
 - ²⁶ M. Mittendorff, T. Winzer, E. Malic, A. Knorr, C. Berger, W. A. de Heer, H. Schneider, M. Helm, and S. Winnerl, *Nano Letters* **14**, 1504 (2014).
 - ²⁷ M. Trushin, A. Grupp, G. Soavi, A. Budweg, D. De Fazio, U. Sassi, A. Lombardo, A. C. Ferrari, W. Belzig, A. Leitenstorfer, and D. Brida, *Phys. Rev. B* **92**, 165429 (2015).
 - ²⁸ L. Fritz, J. Schmalian, M. Müller, and S. Sachdev, *Phys. Rev. B* **78**, 085416 (2008).
 - ²⁹ E. Malic, T. Winzer, E. Bobkin, and A. Knorr, *Phys. Rev. B* **84**, 205406 (2011).
 - ³⁰ M. Trushin and J. Schliemann, *EPL (Europhysics Letters)* **96**, 37006 (2011).
 - ³¹ M. Trushin and J. Schliemann, *Phys. Rev. Lett.* **107**, 156801 (2011).
 - ³² T. J. Echtermeyer, P. S. Nene, M. Trushin, R. V. Gorbachev, A. L. Eiden, S. Milana, Z. Sun, J. Schliemann, E. Lidorikis, K. S. Novoselov, and A. C. Ferrari, *Nano Letters* **14**, 3733 (2014).
 - ³³ C. Jang, S. Adam, J.-H. Chen, E. D. Williams, S. Das Sarma, and M. S. Fuhrer, *Phys. Rev. Lett.* **101**, 146805 (2008).
 - ³⁴ R. Geick, C. H. Perry, and G. Rupprecht, *Phys. Rev.* **146**, 543 (1966).
 - ³⁵ L. Patrick and W. J. Choyke, *Phys. Rev. B* **2**, 2255 (1970).
 - ³⁶ J. M. Dawlaty, S. Shivaraman, M. Chandrashekar, F. Rana, and M. G. Spencer, *Applied Physics Letters* **92**, 042116 (2008).
 - ³⁷ C. H. Lui, K. F. Mak, J. Shan, and T. F. Heinz, *Phys. Rev. Lett.* **105**, 127404 (2010).
 - ³⁸ M. Breusing, S. Kuehn, T. Winzer, E. Malić, F. Milde, N. Severin, J. P. Rabe, C. Ropers, A. Knorr, and T. Elsaesser, *Phys. Rev. B* **83**, 153410 (2011).
 - ³⁹ P. J. Hale, S. M. Horne, J. Moger, D. W. Horsell, and E. Hendry, *Phys. Rev. B* **83**, 121404 (2011).
 - ⁴⁰ J. Shang, T. Yu, J. Lin, and G. G. Gurzadyan, *ACS Nano* **5**, 3278 (2011).
 - ⁴¹ X.-Q. Yan, J. Yao, Z.-B. Liu, X. Zhao, X.-D. Chen, C. Gao, W. Xin, Y. Chen, and J.-G. Tian, *Phys. Rev. B* **90**, 134308 (2014).
 - ⁴² I. Gierz, F. Caglieri, S. Aeschlimann, M. Chávez Cervantes, C. Cacho, R. T. Chapman, E. Springate, S. Link, U. Starke, C. R. Ast, and A. Cavalleri, *Phys. Rev. Lett.* **115**, 086803 (2015).
 - ⁴³ R. Bistritzer and A. H. MacDonald, *Phys. Rev. Lett.* **102**, 206410 (2009).
 - ⁴⁴ I. Goykhman, U. Sassi, B. Desiatov, N. Mazurski, S. Milana, D. de Fazio, A. Eiden, J. Khurgin, J. Shappir, U. Levy, and A. C. Ferrari, *Nano Letters* **16**, 3005 (2016).
 - ⁴⁵ Q. Ma, T. I. Andersen, N. L. Nair, N. M. Gabor, M. Masicotte, C. H. Lui, A. F. Young, W. Fang, K. Watanabe, T. Taniguchi, J. Kong, N. Gedik, F. H. L. Koppens, and P. Jarillo-Herrero, *Nat Phys* **12**, 455 (2016).
 - ⁴⁶ J. F. Rodriguez-Nieva, M. S. Dresselhaus, and L. S. Levitov, *Nano Letters* **15**, 1451 (2015).

- ⁴⁷ F. Bonaccorso, Z. Sun, T. Hasan, and A. C. Ferrari, Nat. Photon. **4**, 611 (2010).
- ⁴⁸ F. H. L. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, and M. Polini, Nat Nano **9**, 780 (2014).